ISGC 2022

N°634 / OC
TOPIC(s) : Waste and side streams valorization / Polymers or composites

A sustainable way of recycling polyamides: dissolution and ammonolysis of polyamides towards diamines and diamides using simple ammonia and biosourced glycerol

AUTHORS

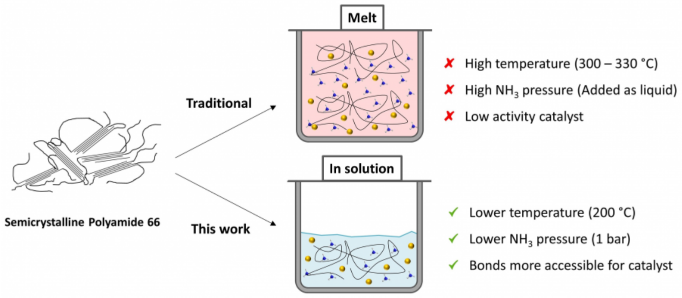
Wouter STUYCK / KU LEUVEN, CELESTIJNENLAAN 200F, LEUVEN
Kwinten JANSSENS / KU LEUVEN, CELESTIJNENLAAN 200F, LEUVEN
Free DE SCHOUWER / KU LEUVEN, CELESTIJNENLAAN 200F, LEUVEN
Robin COECK / KU LEUVEN, CELESTIJNENLAAN 200F, LEUVEN
Corresponding author : Dirk DE VOS / dirk.devos@kuleuven.be

PURPOSE OF THE ABSTRACT

With a production of 380 million metric tons (Mt) in 2015,[1] and a projected growth to 1.124 Mt by the year 2050,[2] it is clear that plastics are indispensable for our current and future modern society. This enormous production however, goes hand in hand with a generation of a large amount of plastic waste, especially because of our longtime take-make-dispose approach of consumable materials. To achieve the transition of the current linear plastics economy to a desirable circular plastics economy, green and environmentally friendly recycling processes must be developed for plastics. Moreover, these recycling processes should be economically feasible, in order to compete with the production of new plastics starting from virgin, petrochemical feedstocks. Polyamide 66 (PA66) can be used in this respect as a potential source for the production of highly valuable, bifunctionalized nitrogen-rich chemicals, due to the presence of the secondary amide bond. However, this secondary amide bond is an intrinsic robust bond, due to its internal resonance stabilization. Moreover, each amide bond participates in two strong hydrogen-bonds with two other polymer chains, which results in a rigid and stable polymer structure represented by its high melting temperature (269 °C). Both characteristics pose severe challenges for the chemical recycling of PA66, which are usually tackled by applying high temperatures (>275 °C),[3,4] supercritical fluids,[5] and/or strong acidic or basic conditions.[6] In this work we report the successful ammonolysis of PA66, which can operate under relatively mild conditions by applying a Lewis acid catalyst and an environmentally friendly glycol solvent (Figure 1). This is a large improvement in greenness compared to traditional ammonolysis processes of PA66, which are performed by melting PA66 at high temperatures (300 °C) and applying ammonia as a liquid.[3] In addition, it is shown that especially the solvent plays a major role to the efficient ammonolysis and that even the use of a bio-based crude glycerol waste stream as a solvent leads to the successful ammonolysis of PA66.

The first aim of this research was to dissolve PA66 at mild temperatures. By dissolving the polymer in a solvent, the secondary amide bonds will be more accessible and therefore more prone to a nucleophilic attack of NH3. With an emphasis on green and environmentally friendly solvents, ethylene glycol was selected, which with its polar and protic properties is able to dissolve PA66 successfully at 180 °C. Subsequently, the ammonolysis of PA66 was conducted in ethylene glycol with 1 bar NH3, which resulted in 36% of broken polyamide bonds after 20 h (Figure 2). To increase this amount, a catalyst screening was performed, which revealed that homogeneous hard Lewis acids perform best. In the case of La(OTf)3, 53% of the polyamide bonds were broken after 20 h. By changing the solvent to glycerol, a remarkable increase of broken polyamide bonds was observed (69% after 20 h), although the concentration of NH3 was nearly equal in both solvents. Remarkably, even in absence of a catalyst, 67% of the polyamide bonds were broken in glycerol. This amount of broken bonds moreover represents the equilibrium of the ammonolysis of PA66 under these conditions, since the reverse reaction (starting from hexamethylenediamine and adipamide) resulted in the same amount of free amines (68%). To explain the high activity of these glycol solvents, we postulate that these solvents possess a proton shuttle effect by forming a hexagonal hydrogen bond transition state [7] and are able to activate NH3 through the formation of a stable 7-ring double hydrogen bond transition state [8]. These findings suggested that crude glycerol obtained from a biorefinery process, could serve as a solvent for the ammonolysis of PA66. To our delight, after a simple filtration, the industrial glycerol sample proved to be an even more suitable solvent for the ammonolysis of PA66.

FIGURES



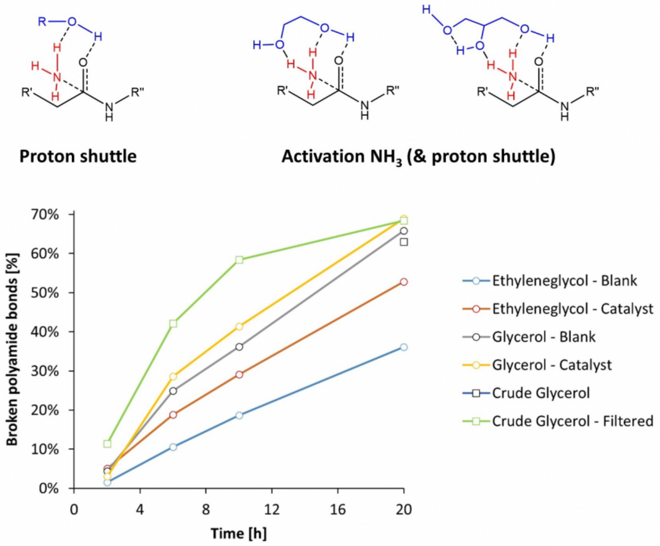


FIGURE 1

Graphical representation of the aim of this work.

Ammonolysis of PA66: Top: state-of-the-art, PA66 melted at high temperatures. Bottom: This work, which aims at a more green ammonolysis process at mild reaction conditions by dissolving PA66 in a solvent.

FIGURE 2

Influence of the solvent on the ammonolysis of PA66. Top: Proton shuttle effect and activation of ammonia. Bottom: Number of broken PA66 bonds over time for different solvents.

Conditions time profiles: 0.1 M PA66 in glycol solvent (10 mL), 200 °C, 1 bar NH3.

KEYWORDS

Polyamides | Plastic recycling | Ammonolysis | Circular economy

---

BIBLIOGRAPHY

[1] Geyer, R., et al. Science Advances, 2017, 3, e170082.

[2] Ellen MacArthur Foundation (2016), The New Plastics Economy: Rethinking the future of plastics. Retrieved from: https://www.ellenmacarthurfoundation.org/.

[3] a) McKinney, R. J. US Pat. 5302756A, 1994. b) McKinney, R. J. US Pat. 5395974A, 1995.

[4] Moran, E. F. J. EP0664787B1, 1995.

[5] Meng, L., et al. Polymer Degrad. Stab., 2004, 83, 389-394.

[6] Song, X., et al. CN107056624A, 2017.

[7] Rangelov, M. A., et al. J. Org. Chem., 2010, 75, 6782-6792.

[8] Gordon, M., et al. J. Am. Chem. Soc., 1949, 71, 1245-1246.